

NOV 29 2011

STATE OF CALIFORNIA  
Department of Toxic Substances ControlPOLLUTION PREVENTION  
& GREEN TECHNOLOGYHealth and Safety Code Section 57019 Chemical Information Call-in Information  
for Nanometals, Nanometal Oxides, and Quantum Dots  
December 2010

This enclosure is provided for your convenience. You may provide the requested information in writing, and attaching any supplementary materials or explanatory information, in letter or report form.

**SECTION A: CHEMICAL(S)** (check each one which applies for your company)

- |  |   |  |
|--|---|--|
| <input type="checkbox"/> Nano Silver           | <input type="checkbox"/> Nano Titanium Dioxide      | <input type="checkbox"/> Nano Cerium Oxide |
| <input type="checkbox"/> Nano Zero Valent Iron | <input checked="" type="checkbox"/> Nano Zinc Oxide | <input type="checkbox"/> Quantum Dot(s)    |

**SECTION B: BUSINESS IDENTIFICATION INFORMATION** (check one and complete items 1 - 10)

- |  |  |  |  |  |
|--|--|--|--|--|
| <input type="checkbox"/> Sole Owner            | <input checked="" type="checkbox"/> Corporation          | <input type="checkbox"/> Limited Liability Company (LLC) | <input type="checkbox"/> Limited Liability Partnership (LLP) | <input type="checkbox"/> Unincorporated Business Trust |
| <input type="checkbox"/> Spouses' Co-ownership | <input type="checkbox"/> Registered Domestic Partnership | <input type="checkbox"/> General Partnership             | <input type="checkbox"/> Limited Partnership                 | <input type="checkbox"/> Other: (describe)             |

1. Name of Sole Owner, Corporation, Partnership, Institution, Other.

BASF Corporation

2. Business Trade Name ("Doing Business As," if any)

3. Business Address (physical location of your business: street number and name, city, state, country, zip or postal code)

100 Campus Drive, Florham Park, NJ 07932

4. Mailing Address (street name and number, P.O. box, city, state, country, zip or postal code, if different from 3)

same as #3

5. Business Website Address(es): www.basf.com

6. Name of Owner, Responsible Corporate Officer, Partner, Other.

7. Contact Information for Person in 6 above.

Name: Raymond M. David, Ph.D.

Title: Manager, Toxicology

Business Telephone: 973-245-6858

Email: raymond.david@basf.com

8. Number of Employees (California employees).

0 - BASF does not manufacture ZnO in California

9. NAICS Code(s) for this business:

Primary:

Other:

Other:

10. Nano Chemical Business Type: (check applicable)

☒ Manufacturer☐ Importer☐ Researcher**SECTION C: CERTIFICATION (FOR THIS COMPLETE SUBMITTAL)**

I am duly authorized to prepare and submit this information, as a formal response to the request pursuant to Health and Safety Code section 57019(d)(1), and certify the information and statements made herein, and in the attachments, are correct to the best of my knowledge and belief.

Name: (type or print)

Raymond M. David

Signature:

R. David

Date:

Oct 4, 2011

**SECTION D: NANOMATERIAL CHEMICAL AND PHYSICAL PROPERTIES** (Attach additional pages as needed)**PRODUCT / PRODUCTION INFORMATION**

NANO CHEMICAL NAME: (Use a separate page for each unique chemical.)	Zinc Oxide
COMMERCIAL NAME(S):	Z-Cote®
ANNUAL PRODUCTION VOLUME:	approx. 225 metric tons
PRODUCTION METHOD(S):	physical vapor synthesis of zinc oxide metal
IDENTIFICATION OF THE SUPPLIER(S):	Nanophase Technologies Corporation

PARAMETER	VALUE / RANGE <sup>1/</sup> (include units)	NAME OF ANALYTICAL METHOD(S) <sup>2/</sup>
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**PHYSICAL PROPERTIES**

SHAPE (MORPHOLOGY)	rod-like, isometric	TEM
DENSITY	not measured	
SURFACE AREA	12 - 24 m <sup>2</sup> /g	specific surface area (BET)
PARTICLE SIZE DISTRIBUTION	Air	
	Liquid	
	Solid / Powder	30-200 nm
OTHER (Specify)		TEM, laser diffraction PSD

**CHEMICAL PROPERTIES**

CHEMICAL COMPOSITION	≥99.0% ZnO	Zinc Oxide USP monograph
SURFACE MODIFICATION (COATING, FUNCTIONALIZATION)	none	
PURITY	meets USP ZnO monograph	
SURFACE CHARGE	not measured	
DISPERSION <sup>3/</sup>	Air	agglomerates of 30-200 nm
	Liquid	agglomerates of 30-200 nm
	Solid	agglomerates of 30-200 nm
IDENTIFYING AND DETERMINING CONCENTRATION OF NANO CHEMICAL, ITS METABOLITES, AND DEGRADATION PRODUCTS IN SPECIFIED MATRICES <sup>4/</sup> Water, Air, Soil, Sediment, Sludge, Chemical Waste, Fish, Blood, Adipose Tissue, Urine, Other (specify)	Please refer to response for section F in the Appendix	
SOLUBILITY	Water Solubility	47 mg/L
	Solubility in Organic Solvent	ICP spectroscopy
N-OCTANOL-WATER PARTITION COEFFICIENT	not applicable	
STABILITY AND REACTIVITY	Flammability	not applicable
	Explosiveness	not applicable
	Oxidizing Properties	not applicable
	Oxidation Reduction Potential	not applicable
	Storage Stability and Reactivity (Container Material)	stable in normal conditions
	Stability to Thermal, Sunlight, and Metal(s)	not applicable

**Notes for Section D:**

Indicate "*Unknown*" if you do not know one of the requested parameters or information items. Indicate "*To Be Developed*" if your company has not yet developed the information. Indicate "*Not Applicable*" only if the specific parameter does not apply for your nano chemical.

1. Specify the *units* (dimensions) for each parameter for which you are reporting values (test results), ranges, and analytical test methods.
2. Specify the *analytical test method(s)* which you currently use for each parameter and report the *value* or *range* for your nano chemical(s). For each method, provide the complete reference (or provide a copy of the complete method). For example, see USEPA 289.2 (1978), ARB Method 310, ASTM E01, OECD 201, as examples of established analytical test methods for chemicals. If you have developed an internal method, or engaged a consultant or external laboratory for a unique or custom test method, provide complete information regarding sample preparation, test protocol(s), limitations, accuracy, precision, bias, required special conditions, resolution limit, applicable matrices, etc. List the consultants, external laboratory personnel, and others with direct knowledge of specialized methods which you have applied for your nano chemical.
3. Describe the extent to which particles agglomerated (i.e., are held together in groups or clusters by attractive inter-particle forces or distribution of particles in the specific system) under "Dispersion."  
**Specify this parameter for three matrices: air, liquid, and solid.**

**SECTION E:**

**Provide a copy of your Globally Harmonized System (GHS) Safety Data Sheet (SDS), if you have prepared one.**

**SECTION F:**

**For each nanomaterial you produce or import, describe the analytical test method(s) that you use, or plan to use, to sample, prepare, and analyze a specific matrix to determine the identify and concentration of each specified nanomaterial. Use a separate page to describe the procedure for each, individual matrix, which must include water, air, soil, sediment, sludge, chemical waste, fish, blood, adipose tissue, and urine. Include the information requested in Section D above.**

## Section E

### Material Safety Data Sheet for Z-Cote®

# Safety Data Sheet

## Z-COTE®

Revision date : 2010/07/29

Page: 1/7

Version: 1.0

(30083071/SDS COS US/EN)

### 1. Product and Company Identification

Use: cosmetic ingredient

Company

BASF CORPORATION  
100 Campus Drive  
Florham Park, NJ 07932, USA

24 Hour Emergency Response Information

CHEMTREC: 1-800-424-9300  
BASF HOTLINE: 1-800-832-HELP

Chemical family:

agglomerates / aggregates of nanoparticles

INCI Name:

Zinc Oxide

### 2. Hazards Identification

Emergency overview**CAUTION:**

PROLONGED OR REPEATED EXPOSURE MAY CAUSE LUNG DAMAGE.

MAY CAUSE RESPIRATORY TRACT IRRITATION.

The product is under certain conditions capable of dust explosion.

Avoid contact with the skin, eyes and clothing.

Avoid inhalation of dusts.

Use with local exhaust ventilation.

Wear a NIOSH-certified (or equivalent) particulate respirator.

Wear safety glasses with side-shields.

Wear chemical resistant protective gloves.

Wear protective clothing.

Eye wash fountains and safety showers must be easily accessible.

State of matter: solid

Colour: white

Odour: odourless

Potential health effects**Primary routes of exposure:**

Routes of entry for solids and liquids include eye and skin contact, ingestion and inhalation. Routes of entry for gases include inhalation and eye contact. Skin contact may be a route of entry for liquified gases.

**Irritation / corrosion:**

Not irritating to the skin. Not irritating to the eyes.

**Sensitization:**

Skin sensitizing effects were not observed in animal studies.

# Safety Data Sheet

## Z-COTE®

Revision date : 2010/07/29  
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(30083071/SDS\_COS\_US/EN)

### Chronic toxicity:

**Repeated dose toxicity:** The substance may cause damage to the lung after repeated inhalation of high doses.

**Genotoxicity:** The substance was not mutagenic in bacteria. The substance was mutagenic in various cell culture test systems; however, these results could not be confirmed in tests with mammals.

### Signs and symptoms of overexposure:

Overexposure may cause: metal fume fever, metallic taste in mouth, tightness in the chest, fever, coughing, headache

### Potential environmental effects

#### Aquatic toxicity:

Very toxic (acute effect) to aquatic organisms.

#### Bioaccumulation / bioconcentration:

The product has not been tested. The statement has been derived from the properties of the individual components.

## 3. Composition / Information on Ingredients

<u>CAS Number</u>	<u>Content (W/W)</u>	<u>Chemical name</u>
1314-13-2	100.0 %	Zinc oxide

## 4. First-Aid Measures

#### General advice:

Remove contaminated clothing.

#### If inhaled:

Remove the affected individual into fresh air and keep the person calm. Assist in breathing if necessary. Immediate medical attention required.

#### If on skin:

Wash affected areas thoroughly with soap and water. If irritation develops, seek medical attention.

#### If in eyes:

Flush with copious amounts of water for at least 15 minutes. If irritation develops, seek medical attention.

#### If swallowed:

Immediately rinse mouth and then drink plenty of water, do not induce vomiting, seek medical attention. Never induce vomiting or give anything by mouth if the victim is unconscious or having convulsions.

#### Note to physician

Treatment: Symptomatic treatment (decontamination, vital functions).

## 5. Fire-Fighting Measures

#### Flash point:

The substance/product is non-combustible.  
not applicable

#### Flammability:

does not ignite

#### Self-ignition temperature:

not self-igniting  
(other) not self-igniting

#### Suitable extinguishing media:

water spray, carbon dioxide, foam, dry powder

# Safety Data Sheet

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**Protective equipment for fire-fighting:**

Firefighters should be equipped with self-contained breathing apparatus and turn-out gear.

**Further information:**

Dispose of fire debris and contaminated extinguishing water in accordance with official regulations.

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## 6. Accidental release measures

**Personal precautions:**

Ensure adequate ventilation. Wear appropriate respiratory protection.

**Environmental precautions:**

Do not discharge into drains/surface waters/groundwater.

**Cleanup:**

Dispose of absorbed material in accordance with regulations.

For small amounts: Sweep/shovel up.

For large amounts: Sweep/shovel up.

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## 7. Handling and Storage

**Handling****General advice:**

Avoid dust formation. Avoid aerosol formation. Don't mill the product in a dry form.

**Protection against fire and explosion:**

Prevent electrostatic charge - sources of ignition should be kept well clear - fire extinguishers should be kept handy. Avoid dust formation.

**Storage****General advice:**

Keep container tightly closed in a cool, well-ventilated place.

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## 8. Exposure Controls and Personal Protection

**Advice on system design:**

Provide local exhaust ventilation to control dust.

**Personal protective equipment****Respiratory protection:**

Wear a NIOSH-certified (or equivalent) particulate respirator.

**Hand protection:**

Wear chemical resistant protective gloves., Consult with glove manufacturer for testing data.

**Eye protection:**

Safety glasses with side-shields.

**Body protection:**

Body protection must be chosen based on level of activity and exposure.

**General safety and hygiene measures:**

Avoid contact with eyes. Avoid inhalation of dusts. Handle in accordance with good industrial hygiene and safety practice.

# Safety Data Sheet

## Z-COTE®

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(30083071/SDS\_COS\_US/EN)

### 9. Physical and Chemical Properties

Form:	powder, solid	
Odour:	odourless	
Colour:	white	
pH value:	approx. 7	( 50 g/l, 20 °C) (as suspension)
Melting point:	approx. 1,970 °C	
Vapour pressure:		( 20 °C) negligible
Bulk density:	approx. 500 - 700 kg/m <sup>3</sup>	Literature data.
Partitioning coefficient n-octanol/water (log Pow):		not applicable
Particle size:		Contains agglomerates / aggregates of nanoparticles
Solubility in water:	1.5 g/l	
Molar mass:	81.39 g/mol	
Other Information:	primary particle size < 200 nm	

### 10. Stability and Reactivity

**Substances to avoid:**  
hydrogen peroxide, magnesium

**Hazardous reactions:**  
No hazardous reactions if stored and handled as prescribed/indicated.

**Thermal decomposition:**  
No decomposition if used as directed.

### 11. Toxicological information

#### Acute toxicity

**Oral:**  
Type of value: LD50  
Species: rat  
Value: > 5,000 mg/kg  
Literature data.

**Inhalation:**  
Type of value: LC50  
Species: rat (male/female)  
Value: > 5.7 mg/l (BASF-Test)  
Exposure time: 4 h

#### Irritation / corrosion

**Skin:**  
Species: rabbit  
Result: non-irritant  
Literature data.

**Eye:**  
Species: rabbit  
Result: non-irritant



# Safety Data Sheet

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**Sensitization:**

Guinea pig maximization test

Species: guinea pig

Result: Non-sensitizing.

Method: OECD Guideline 406

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## 12. Ecological Information

### Fish

Acute:

static

Oncorhynchus mykiss/LC50 (96 h): 0.14 mg/l

Literature data.

Chronic:

Flow through.

Jordanella floridae /NOEC (98 d): 0.051 mg/l

### Aquatic invertebrates

Acute:

static

Daphnia magna/EC50 (48 h): 2.2 mg/l

Chronic:

Flow through. See user defined text. 28 d 0.025 mg/l

### Aquatic plants

Toxicity to aquatic plants:

static

green algae/EC50 (72 h): 0.17 mg/l

### Microorganisms

Toxicity to microorganisms:

bacterium/EC0 (16 h): > 80,000 mg/l

### Degradability / Persistence

#### Biological / Abiological Degradation

Evaluation:

Inorganic product which cannot be eliminated from water by biological purification processes.

### Bioaccumulation

mayfly Bioconcentration factor 1,130

flagfish Bioconcentration factor 432

marine algae Bioconcentration factor 4,680

marine algae Bioconcentration factor 16,600

oyster Bioconcentration factor 16,700

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## 13. Disposal considerations

### Waste disposal of substance:

Do not discharge into waterways or sewer systems without proper authorization. Dispose of in accordance with national, state and local regulations.

### Container disposal:

Dispose of container and any rinsate in an environmentally safe manner. Recommend crushing, puncturing or other means to prevent unauthorized use of used containers.

# Safety Data Sheet

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### 14. Transport Information

**Land transport**

USDOT

Not classified as a dangerous good under transport regulations

**Sea transport**

IMDG

Hazard class: 9  
Packing group: III  
ID number: UN 3077  
Hazard label: 9, EHSM  
Marine pollutant: YES  
Proper shipping name: ENVIRONMENTALLY HAZARDOUS SUBSTANCE, SOLID, N.O.S.  
(contains ZINC OXIDE)

**Air transport**

IATA/ICAO

Hazard class: 9  
Packing group: III  
ID number: UN 3077  
Hazard label: 9, EHSM  
Proper shipping name: ENVIRONMENTALLY HAZARDOUS SUBSTANCE, SOLID, N.O.S.  
(contains ZINC OXIDE)

### 15. Regulatory Information

**Federal Regulations****Registration status:**

Chemical TSCA, US released / listed

Cosmetic TSCA, US released / exempt

OSHA hazard category: OSHA PEL established; Toxic - inhalation

EPCRA 311/312 (Hazard categories): Acute;

**EPCRA 313:**

<u>CAS Number</u>	<u>Chemical name</u>
1314-13-2	Zinc oxide
50 LBS	

**State regulations**

<u>State RTK</u>	<u>CAS Number</u>	<u>Chemical name</u>
MA, NJ, PA	1314-13-2	Zinc oxide

# Safety Data Sheet

## Z-COTE®

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### 16. Other Information

**NFPA Hazard codes:**

Health : 1

Fire: 1

Reactivity: 0

Special:

**HMIS III rating**

Health: 1

Flammability: 1

Physical hazard: 0

NFPA and HMIS use a numbering scale ranging from 0 to 4 to indicate the degree of hazard. A value of zero means that the substance possesses essentially no hazard; a rating of four indicates extreme danger. Although similar, the two rating systems are intended for different purposes, and use different criteria. The NFPA system was developed to provide an on-the-spot alert to the hazards of a material, and their severity, to emergency responders. The HMIS system was designed to communicate workplace hazard information to employees who handle hazardous chemicals.

We support worldwide Responsible Care® initiatives. We value the health and safety of our employees, customers, suppliers and neighbors, and the protection of the environment. Our commitment to Responsible Care is integral to conducting our business and operating our facilities in a safe and environmentally responsible fashion, supporting our customers and suppliers in ensuring the safe and environmentally sound handling of our products, and minimizing the impact of our operations on society and the environment during production, storage, transport, use and disposal of our products.

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**MSDS Prepared by:**

BASF NA Product Regulations

msds@basf.com

MSDS Prepared on: 2010/07/29

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END OF DATA SHEET

## **SECTION F.**

### **Test Methods Referenced in this Submission**

**Surface Area** – BET surface area determination by DIN-66131

**Particle Size Distribution** – BASF internal test method *PM-00806* (Trade Secret)

**Chemical Composition** - “Zinc Oxide” Monograph – USP 34

**Purity** – “Zinc Oxide” Monograph – USP 34

**Water Solubility** – Umicore internal test “*Solubility of four ZnO samples*” (Trade Secret)

**Literature citations relevant to environmental concentrations of ZnO**

**Surface Area – BET surface area determination by DIN/ISO 9277:2010**

ISO 9277:2010 specifies the determination of the overall specific external and internal surface area of disperse (e.g. nano-powders) or porous solids by measuring the amount of physically adsorbed gas according to the Brunauer, Emmett and Teller (BET) method. It takes account of the International Union for Pure and Applied Chemistry (IUPAC) recommendations of 1984 and 1994.

The BET method is applicable only to adsorption isotherms of type II (disperse, nonporous or macroporous solids) and type IV (mesoporous solids, pore diameter between 2 nm and 50 nm). Inaccessible pores are not detected. The BET method cannot reliably be applied to solids which absorb the measuring gas.

A strategy for specific surface area determination of microporous materials (type I isotherms) is described in an annex.

Available for purchase at

<http://webstore.ansi.org/RecordDetail.aspx?sku=ISO+9277%3a2010>

**THE FOLLOWING 14 PAGES ARE CONSIDERED TRADE SECRET**

## Zinc Gluconate Tablets

### DEFINITION

Zinc Gluconate Tablets contain NLT 93.0% and NMT 107.0% of the labeled amount of Zn, in the form of zinc gluconate ( $C_{12}H_{22}O_{14}Zn$ ).

### IDENTIFICATION

#### • A. THIN-LAYER CHROMATOGRAPHY

**Standard solution:** USP Potassium Gluconate RS in water; 10 mg/mL

**Sample solution:** Transfer a weighed quantity of powdered Tablets to a suitable flask, and add the necessary volume of water to obtain a solution containing about 10 mg/mL of zinc gluconate. Shake and sonicate, heating in a water bath at 60°, if necessary, and filter.

#### Chromatographic system

(See *Chromatography* <621>, *Thin-Layer Chromatography*.)

**Mode:** TLC

**Adsorbent:** 0.25-mm layer of chromatographic silica gel

**Application volume:** 5  $\mu$ L

**Developing solvent system:** Alcohol, water, ammonium hydroxide, and ethyl acetate (50:30:10:10)

**Spray reagent:** Dissolve 2.5 g of ammonium molybdate in about 50 mL of 2 N sulfuric acid in a 100-mL volumetric flask, add 1.0 g of ceric sulfate, swirl to dissolve, dilute with 2 N sulfuric acid to volume, and mix.

#### Analysis

**Samples:** *Standard solution* and *Sample solution*

When the solvent front has moved about three-fourths the length of the plate, remove the plate from the chamber, and dry at 110° for 20 min. Allow to cool, spray with *Spray reagent*, and heat the plate at 110° for about 10 min.

**Acceptance criteria:** The principal spot from the *Sample solution* corresponds in color, size, and  $R_f$  value to that from the *Standard solution*.

#### • B. PROCEDURE

**Sodium hydroxide solution:** 42 mg/mL of sodium hydroxide

**Ammonium chloride solution:** 107 mg/mL of ammonium chloride

**Glycerin solution:** A mixture of glycerin and water (85:15)

**Sodium sulfide solution:** Dissolve 12 g of sodium sulfide with heating in a 45-mL mixture of *Glycerin solution* and water (29:10), allow to cool, and dilute with the same mixture of solvents to 100 mL. The solution should be colorless.

**Sample solution:** Shake and sonicate the amount of powdered Tablets with the necessary volume of water to obtain a solution containing 100 mg/mL of zinc gluconate. Heat in a water bath at 60°, if necessary, and filter.

**Analysis:** To 5 mL of the *Sample solution* add 0.2 mL of *Sodium hydroxide solution*, add an additional 2 mL of *Sodium hydroxide solution*, and add 10 mL of *Ammonium chloride solution*. Add 0.1 mL of *Sodium sulfide solution*.

**Acceptance criteria:** A white precipitate is formed after the first addition of *Sodium hydroxide solution*. The precipitate dissolves after the second addition of *Sodium hydroxide solution*. The solution remains clear after addition of *Ammonium chloride solution*, and a white precipitate forms after addition of *Sodium sulfide solution*.

### STRENGTH

#### • PROCEDURE

**Sample solution:** Weigh and finely powder NLT 20 Tablets. Weigh a portion of the powder, equivalent to about 80 mg of zinc, transfer to a suitable crucible, and ignite, gently at first, until free from carbon. Cool the crucible, add 25 mL of water and 5 mL of hydrochloric acid, and stir. Heat on a steam bath for 5 min, and filter, rinsing the filter with several portions of water. Dilute the combined filtrate and washes with water to about 100 mL.

**Analysis:** Add ammonia–ammonium chloride buffer TS until the solution is neutral to litmus. Add 5 mL of ammonia–am-

monium chloride buffer TS and 0.1 mL of eriochrome black TS, and titrate with 0.05 M edetate disodium VS to a blue endpoint. Each mL of 0.05 M edetate disodium is equivalent to 3.27 mg of Zn or 22.78 mg of zinc gluconate ( $C_{12}H_{22}O_{14}Zn$ ).

**Acceptance criteria:** 93.0%–107.0%

### PERFORMANCE TESTS

• **DISINTEGRATION** <701>: For Tablets intended to be mixed with water prior to intake as oral liquids  
**Time:** NMT 60 s

• **DISINTEGRATION AND DISSOLUTION OF DIETARY SUPPLEMENTS** <2040>: For Tablets not to be mixed with water prior to ingestion

**Medium:** Hydrochloric acid 0.01 N; 900 mL

**Apparatus 2:** 50 rpm

**Time:** 45 min

**Analysis:** Determine the amount of  $C_{12}H_{22}O_{14}Zn$  dissolved, employing atomic absorption spectrophotometry at the resonance emission line for zinc, at 213.8 nm, on filtered portions of the solution under test, suitably diluted with water, in comparison with a standard solution having a known concentration of zinc in the same *Medium*.

**Tolerances:** NLT 75% of the labeled amount of  $C_{12}H_{22}O_{14}Zn$  is dissolved.

• **UNIFORMITY OF DOSAGE UNITS** <905>: Meet the requirements

### ADDITIONAL REQUIREMENTS

• **PACKAGING AND STORAGE:** Preserve in tight containers, protected from light.

• **LABELING:** Label the Tablets in terms of elemental zinc, and also in terms of zinc gluconate ( $C_{12}H_{22}O_{14}Zn$ ). The labeling indicates whether the Tablets are intended to be mixed with water before intake.

• **USP REFERENCE STANDARDS** <11>  
USP Potassium Gluconate RS

## Zinc Oxide

ZnO 81.39

Zinc oxide.

Zinc oxide [1314-13-2].

» Zinc Oxide, freshly ignited, contains not less than 99.0 percent and not more than 100.5 percent of ZnO.

**Packaging and storage**—Preserve in well-closed containers.

#### Identification—

A: When strongly heated, it assumes a yellow color that disappears on cooling.

B: A solution of it in a slight excess of 3 N hydrochloric acid responds to the tests for *Zinc* <191>.

**Alkalinity**—Mix 1.0 g with 10 mL of hot water, add 2 drops of phenolphthalein TS, and filter: if a red color is produced, not more than 0.30 mL of 0.10 N hydrochloric acid is required to discharge it.

**Loss on ignition** <733>—Weigh accurately about 2 g, and ignite at 500° to constant weight: it loses not more than 1.0% of its weight.

**Carbonate and color of solution**—Mix 2.0 g with 10 mL of water, add 30 mL of 2 N sulfuric acid, and heat on a steam bath, with constant stirring: no effervescence occurs and the resulting solution is clear and colorless.

**Arsenic**, *Method I* <211>: 6 ppm.

**Lead**—Add 2 g to 20 mL of water, stir well, add 5 mL of glacial acetic acid, and warm on a steam bath until solution is effected: the addition of 5 drops of potassium chromate TS produces no turbidity or precipitate.

**Iron and other heavy metals**—Cool two separate 5-mL portions of the solution obtained in the test for *Carbonate and color of solution*. White precipitates are formed when potassium ferrocyanide TS is added to the first portion and when sodium sulfide TS is added to the second portion.

**Assay**—Dissolve about 1.5 g of freshly ignited Zinc Oxide, accurately weighed, and 2.5 g of ammonium chloride in 50.0 mL of 1 N sulfuric acid VS with the aid of gentle heat, if necessary. When solution is complete, add methyl orange TS, and titrate the excess sulfuric acid with 1 N sodium hydroxide VS. Each mL of 1 N sulfuric acid is equivalent to 40.69 mg of ZnO.

## Zinc Oxide Neutral

ZnO 81.39

» Zinc Oxide Neutral, freshly ignited, contains not less than 95.0 percent and not more than 98.0 percent of ZnO.

**Packaging and storage**—Preserve in well-closed containers, and store at controlled room temperature.

**Labeling**—Label it to indicate that it is for use in sunscreen preparations only.

### Identification—

**A:** When strongly heated, it assumes a yellow color that disappears on cooling.

**B:** A solution of it in a slight excess of 3 N hydrochloric acid responds to the tests for *Zinc* (191).

**Alkalinity**—Mix 1.0 g with 10 mL of hot water. The addition of two drops of phenolphthalein TS produces no color change.

**Loss on ignition** (733)—Weigh accurately about 1 g, and ignite at 750° for 15 minutes: it loses not more than 5.0% of its weight.

**Carbonate and color of solution**—Mix 2.0 g with 10 mL of water, add 30 mL of 2 N sulfuric acid, and heat on a steam bath with constant stirring: no effervescence occurs, and the resulting solution is clear and colorless. [NOTE—Use this solution in the test for *Iron and other heavy metals*.]

**Sulfate** (221)—A 0.1 g portion shows no more sulfate than corresponds to 2.3 mL of 0.020 N sulfuric acid (2.2%).

**Arsenic, Method I** (211): 2 ppm.

**Lead**—Add 2 g to 20 mL of water, stir well, add 5 mL of glacial acetic acid, and warm on a steam bath until solution is effected: the addition of five drops of potassium chromate TS produces no turbidity or precipitate.

### Mercury—

*Mercury Detection Instrument and Aeration Apparatus*—Proceed as directed for the section *Method IIa and Method IIb* under *Mercury* (261).

*Nitric acid solution 1*—Carefully add 50 mL of nitric acid to 450 mL of water, and mix.

*Nitric acid solution 2*—Carefully add 10 mL of nitric acid to 490 mL of water, and mix.

*Hydrochloric acid–nitric acid solution*—Carefully add three volumes of concentrated hydrochloric acid to one volume of concentrated nitric acid. [NOTE—Prepare immediately before use.]

*Stannous sulfate solution*—Add 25 g of stannous sulfate to 250 mL of 0.5 N sulfuric acid. [NOTE—The mixture is a suspension and should be stirred continuously during use.]

*Sodium chloride–hydroxylamine sulfate solution*—Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in water, dilute with water to 100 mL, and mix.

*Potassium permanganate solution*—Dissolve 5 g of potassium permanganate in 100 mL of water, and mix.

*Standard stock mercury solution*—Dissolve 0.1354 g of mercuric chloride in *Nitric acid solution 1* to obtain a solution having a concentration of about 1.0 mg of mercury per mL. [NOTE—Use of a commercially prepared mercury standard is recommended.]

*Standard working mercury solution*—Quantitatively dilute an accurately measured volume of the *Standard stock mercury solution* with *Nitric acid solution 2* to obtain a solution having a known concentration of about 0.5 µg of mercury per mL.

*Standard solutions*—Transfer 1-, 2-, 3-, and 4-mL aliquots of *Standard stock mercury solution* to four separate 300-mL biological oxygen-demand (BOD) bottles. To each bottle, add 5 mL of water and 5 mL of *Hydrochloric acid–nitric acid solution*. Heat the sample for 2 minutes in a water bath at 95°. Cool, and add 50 mL of water and 15 mL of *Potassium permanganate solution*. Mix thoroughly, and place in a water bath for 30 minutes at 95°. Cool, add 5 mL of *Sodium chloride–hydroxylamine sulfate solution*, dilute with water to 200 mL, and mix. These solutions contain the equivalents of 2.5, 5, 7.5, and 10 ng of mercury per mL, respectively.

*Blank solution*—To a 300-mL BOD bottle, add 5 mL of water and 5 mL of *Hydrochloric acid–nitric acid solution*. Heat the solution for 2 minutes in a water bath at 95°. Cool, and add 50 mL of water and 15 mL of *Potassium permanganate solution*. Mix thoroughly, and place in a water bath for 30 minutes at 95°. Cool, add 5 mL of *Sodium chloride–hydroxylamine sulfate solution*, dilute with water to 200 mL, and mix.

*Test solution*—Transfer about 2.0 g of Zinc Oxide Neutral, accurately weighed, to a 300-mL BOD bottle. To the bottle, add 5 mL of water and 5 mL of *Hydrochloric acid–nitric acid solution*. Heat the sample in a water bath for 2 minutes at 95°. Cool, and add 50 mL of water and 15 mL of *Potassium permanganate solution*. Mix thoroughly, and place in a water bath for 30 minutes at 95°. Cool, add 5 mL of *Sodium chloride–hydroxylamine sulfate solution*, dilute with water to 200 mL, and mix.

*Procedure*—Add 5 mL of *Stannous sulfate solution* to a *Standard solution*, and immediately insert the bottle into the *Aeration Apparatus*. Obtain the absorbance of the *Standard solution*. Repeat with the remaining *Standard solutions*, *Test solution*, and *Blank solution*. Perform a blank determination, and make any necessary corrections. Plot the absorbances of the *Standard solutions* versus concentrations, in µg per mL, and draw the straight line best fitting the plotted points. From the graph so obtained, determine the concentration, in µg per g of mercury, in the *Test solution*: not more than 1 µg per g is found.

**Iron and other heavy metals**—Cool two separate 5-mL portions of the solution obtained in the test for *Carbonate and color of solution*. White precipitates are formed when potassium ferrocyanide TS is added to the first portion and when sodium sulfide TS is added to the second portion.

### Content of magnesium oxide—

*Nitric acid solution*—Carefully add 10 mL of concentrated nitric acid to 490 mL of water, and mix.

*Standard solution*—Prepare a solution in *Nitric acid solution* having a concentration of about 25 µg of magnesium per mL. [NOTE—Use of a commercially prepared magnesium–inductively coupled plasma standard solution is recommended.]

*Test solution*—Transfer 200 mg of Zinc Oxide Neutral, accurately weighed, to a 50-mL volumetric flask. Dissolve in and dilute with *Nitric acid solution* to volume.

*Procedure*—Set up an inductively coupled plasma–atomic emission spectrometer with a wavelength of 279.1 nm, RF power of about 1.2 KW, argon torch flow of about 17 L per minute, argon nebulizer flow of about 1.0 L per minute, and argon auxiliary flow of about 1.4 L per minute. Analyze the *Standard solution* and *Test solution*, using *Nitric acid solution* as the blank. Calculate the percentage of magnesium oxide in the portion of Zinc Oxide Neutral taken by the formula:

$$5FC/W$$

in which *F* is the conversion factor for conversion of magnesium to magnesium oxide (1.658); *C* is the concentration, in µg per



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**Langmuir.** 2011 May 17;27(10):6059-68. Epub 2011 Apr 18.

Aggregation and dissolution of 4 nm ZnO nanoparticles in aqueous environments: influence of pH, ionic strength, size, and adsorption of humic acid.

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Metal oxide nanoparticles are used in a wide range of commercial products, leading to an increased interest in the behavior of these materials in the aquatic environment. The current study focuses on the stability of some of the smallest ZnO nanomaterials,  $4 \pm 1$  nm in diameter nanoparticles, in aqueous solutions as a function of pH and ionic strength as well as upon the adsorption of humic acid. Measurements of nanoparticle aggregation due to attractive particle-particle interactions show that ionic strength, pH, and adsorption of humic acid affect the aggregation of ZnO nanoparticles in aqueous solutions, which are consistent with the trends expected from Derjaguin-Landau-Verwey-Overbeek (DLVO) theory. Measurements of nanoparticle dissolution at both low and high pH show that zinc ions can be released into the aqueous phase and that humic acid under certain, but not all, conditions can increase  $\text{Zn}^{2+}(\text{aq})$  concentrations. Comparison of the dissolution of ZnO nanoparticles of different nanoparticle diameters, including those near 15 and 240 nm, shows that the smallest nanoparticles dissolve more readily. Although qualitatively this enhancement in dissolution can be predicted by classical thermodynamics, quantitatively it does not describe the dissolution behavior very well.

**Environ Sci Technol.** 2011 Apr 1;45(7):2826-32. Epub 2011 Mar 7.

Effects of ZnO nanoparticles on wastewater biological nitrogen and phosphorus removal.

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With the increasing utilization of nanomaterials, zinc oxide nanoparticles (ZnO NPs) have been reported to induce adverse effects on human health and aquatic organisms. However, the potential impacts of ZnO NPs on wastewater nitrogen and phosphorus removal with an activated sludge process are unknown. In this paper, short-term exposure experiments were conducted to determine whether ZnO NPs caused adverse impacts on biological nitrogen and phosphorus removal in the unacclimated anaerobic-low dissolved oxygen sequencing batch reactor. Compared with the absence of ZnO NPs, the presence of 10 and 50 mg/L of ZnO NPs decreased total nitrogen removal efficiencies from 81.5% to 75.6% and 70.8%, respectively. The corresponding effluent phosphorus concentrations increased from nondetectable to 10.3 and 16.5 mg/L, respectively, which were higher than the influent phosphorus (9.8 mg/L), suggesting that higher concentration of ZnO NPs induced the loss of normal phosphorus removal. It was found that the inhibition of

nitrogen and phosphorus removal induced by higher concentrations of ZnO NPs was due to the release of zinc ions from ZnO NPs dissolution and increase of reactive oxygen species (ROS) production, which caused inhibitory effect on polyphosphate-accumulating organisms and decreased nitrate reductase, exopolyphosphatase, and polyphosphate kinase activities.

**J Hazard Mater.** 2011 Jan 30;185(2-3):1131-9. Epub 2010 Oct 14.

Preconcentration and separation of copper, nickel and zinc in aqueous samples by flame atomic absorption spectrometry after column solid-phase extraction onto MWCNTs impregnated with D2EHPA-TOPO mixture.

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A solid phase extraction method has been developed for the determination of copper, nickel and zinc ions in natural water samples. This method is based on the adsorption of copper, nickel and zinc on multiwalled carbon nanotubes (MWCNTs) impregnated with di-(2-ethyl hexyl phosphoric acid) (D2EHPA) and tri-n-octyl phosphine oxide (TOPO). The influence of parameters such as pH of the aqueous solution, amount of adsorbent, flow rates of the sample and eluent, matrix effects and D2EHPA-TOPO concentration have been investigated. Desorption studies have been carried out with 2 mol L<sup>-1</sup> HNO<sub>3</sub>. The copper, nickel and zinc concentrations were determined by flame atomic absorption spectrometry. The results indicated that the maximum adsorption of copper, nickel and zinc is at pH 5.0 with 500 mg of MWCNTs. The detection limits by three sigma were 50 µg L<sup>-1</sup> for copper, 40 µg L<sup>-1</sup> for nickel and 60 µg L<sup>-1</sup> zinc. The highest enrichment factors were found to be 25. The adsorption capacity of MWCNTs-D2EHPA-TOPO was found to be 4.90 mg g<sup>-1</sup> for copper, 4.78 mg g<sup>-1</sup> for nickel and 4.82 mg g<sup>-1</sup> for zinc. The developed method was applied for the determination of copper, nickel and zinc in electroplating wastewater and real water sample with satisfactory results (R.S.D.'s <10%).

**Environ Sci Technol.** 2010 Nov 1;44(21):8314-21.

Nanometals induce stress and alter thyroid hormone action in amphibia at or below North American water quality guidelines.

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Nanometals are manufactured to particle sizes with diameters in the nanometer range and are included in a variety of consumer and health products. There is a lack of information regarding potential effects of these materials on aquatic organisms. Amphibians are regarded as environmental sentinels and demonstrate an

exquisite sensitivity to thyroid hormone action, a hormone that is essential for human health. This present study assessed the effect of exposure to nanometals on stress and thyroid hormone signaling in frog tissue using a cultured tail fin biopsy (C-fin) assay derived from *Rana catesbeiana* tadpoles. The C-fin assay maintains tissue complexity and biological replication while multiple chemical responses can be assessed from the same individual. We tested the ability of nanosilver (0.06  $\mu\text{g/L}$ -5.5 mg/L), quantum dots (0.25  $\mu\text{g/L}$ -22 mg/L), and nanozinc oxide (0.19-10 mg/L) to alter gene expression in the presence or absence of 3,3',5'-triiodothyronine (T(3)) using quantitative real-time polymerase chain reaction. Results were compared to exposure to micrometer-silver, silver nitrate, and micrometer-cadmium telluride. Nanosilver ( $\geq 2.75$  mg/L) and quantum dots ( $\geq 0.22$  mg/L) altered the expression of transcripts linked to T(3)- and stress-mediated pathways, while nanozinc oxide had no effect. Lower concentrations of nanosilver (0.6 to 550  $\mu\text{g/L}$ ) perturbed T(3)-mediated signaling while not inducing cell stress. The observed effects were orders of magnitude below acute toxicity levels and occurred at or below the current North American water quality guidelines for metals, underscoring the need for evaluating nanoparticles separately from their constituent chemicals.

**Environ Sci Technol.** 2009 Dec 15;43(24):9216-22.

Modeled environmental concentrations of engineered nanomaterials (TiO(2), ZnO, Ag, CNT, Fullerenes) for different regions.

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Engineered nanomaterials (ENM) are already used in many products and consequently released into environmental compartments. In this study, we calculated predicted environmental concentrations (PEC) based on a probabilistic material flow analysis from a life-cycle perspective of ENM-containing products. We modeled nano-TiO(2), nano-ZnO, nano-Ag, carbon nanotubes (CNT), and fullerenes for the U.S., Europe and Switzerland. The environmental concentrations were calculated as probabilistic density functions and were compared to data from ecotoxicological studies. The simulated modes (most frequent values) range from 0.003 ng L<sup>-1</sup> (fullerenes) to 21 ng L<sup>-1</sup> (nano-TiO(2)) for surface waters and from 4 ng L<sup>-1</sup> (fullerenes) to 4 microg L<sup>-1</sup> (nano-TiO(2)) for sewage treatment effluents. For Europe and the U.S., the annual increase of ENMs on sludge-treated soil ranges from 1 ng kg<sup>-1</sup> for fullerenes to 89 microg kg<sup>-1</sup> for nano-TiO(2). The results of this study indicate that risks to aquatic organisms may currently emanate from nano-Ag, nano-TiO(2), and nano-ZnO in sewage treatment effluents for all considered regions and for nano-Ag in surface waters. For the other environmental compartments for which ecotoxicological data were available, no risks to organisms are presently expected.

**Sci Total Environ.** 2009 Apr 1;407(8):2919-30. Epub 2009 Jan 22.

Heavy metal mobility in intertidal sediments of the Scheldt estuary: Field monitoring.

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The current paper aims to check whether the factors affecting metal mobility in intertidal sediments and floodplain soils of the river Scheldt, as identified under controlled greenhouse conditions in previous studies, also play a similar role under variable field conditions. Moreover, we aimed to assess the importance of these factors as a function of sampling time and depth, with respect to the natural variations in water table levels. This field monitoring revealed that the mobility of metals in intertidal sediments of the Scheldt estuary indeed are affected by factors which were identified to affect the metal fate in the upper sediment layer in previous greenhouse experiments. However, the effects were often less pronounced under field conditions. This can be attributed to the lower sampling resolution, the occurrence of interactions between factors, the disturbance of microbial communities during setup of greenhouse experiments and the more moderate environmental conditions in the field, affecting microbial and enzymatic activities. At most of the sampled wetlands, the level of the water table fluctuated only slightly during fall, winter and spring, whereas it decreased substantially during summer, especially at the sites with more sandy sediments. The highest sulphide concentrations were found at the sites where the water table level never decreased considerably. These sulphides primarily suppress the availability of Cd, Cu, Ni and Zn. Organic complexation resulted in the mobilisation of Cu, Ni and Cr. The concentrations of Cd, Ni and Zn in the pore water were affected by Fe/Mn oxide reduction, whereas Cd and Zn concentrations appeared to be also affected by the salinity.

**Environ Geochem Health.** 2008 Dec;30(6):549-63. Epub 2008 Jun 18.

Bioavailability of trace metals in brownfield soils in an urban area in the UK.

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Thirty-two brownfield sites from the city of Wolverhampton were selected from those with a former industrial use, wasteland or areas adjacent to industrial processes. Samples (<2 mm powdered soil fraction) were analysed, using inductively coupled plasma-atomic emission spectrometry (ICP-AES) for 20 elements. Loss on ignition and pH were also determined. A five-step chemical sequential extraction technique was carried out. Single leach extraction with 0.12 M hydrochloric acid of Pb, Cu and Zn in soil was determined as a first approximation of the bioavailability in the human stomach. Some of the sites were

found to have high concentrations of the potentially toxic elements Pb, Zn, Cu and Ni. The partitioning of metals showed a high variability, however a number of trends were determined. The majority of Zn was partitioned into the least chemically stable phases (steps 1, 2 and 3). The majority of Cu was associated with the organic phase (step 4) and the majority of Ni was fractionated into the residue phase (step 5). The majority of Pb was associated with the residue fraction (step 5) followed by Fe-Mn oxide fraction (step 3). The variability reflects the heterogeneous and complex nature of metal speciation in urban soils with varied historic histories. There was a strong inverse linear relationship between the metals Ni, Zn and Pb in the readily exchangeable phase (step 1) and soil pH, significant at  $P < 0.01$  level. There was a significant increase ( $P < 0.05$ ) in the partitioning of Cu, Ni and Zn into step 4 (the organic phase) in soils with a higher organic carbon content (estimated by loss on ignition). Copper was highly partitioned into step 4 as it has a strong association with organics in soil but this phase was not important for the partitioning of Ni or Zn. The fractionation of Ni, Cu and Zn increased significantly in step 3 when the total metal concentration increases ( $P < 0.01$ ). The Fe-Mn oxide fraction becomes more important in soils elevated in these metals, possibly due to the scavenging of metals by oxides. Cu and Pb extracted by HCl was statistically similar to the sum of the metals in steps 1 to 4 ( $P < 0.01$ ) and HCl available Zn was statistically similar to the sum of Zn in steps 1 to 3 ( $P < 0.01$ ). Step 4 (the organic phase) was not an important phase for Zn, so it was concluded that any Cu, Zn and Pb present in soil in a nonresidue phase would be potentially available for uptake into the human system once soil has been ingested.

**Water Res.** 2008 Jun;42(12):3135-45. Epub 2008 Mar 18.

Observed and modeled seasonal trends in dissolved and particulate Cu, Fe, Mn, and Zn in a mining-impacted stream.

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North Fork Clear Creek (NFCC) in Colorado, an acid-mine drainage (AMD) impacted stream, was chosen to examine the distribution of dissolved and particulate Cu, Fe, Mn, and Zn in the water column, with respect to seasonal hydrologic controls. NFCC is a high-gradient stream with discharge directly related to snowmelt and strong seasonal storms. Additionally, conditions in the stream cause rapid precipitation of large amounts of hydrous iron oxides (HFO) that sequester metals. Because AMD-impacted systems are complex, geochemical modeling may assist with predictions and/or confirmations of processes occurring in these environments. This research used Visual-MINTEQ to determine if field data collected over a two and one-half year study would be well represented by modeling with a currently existing model, while limiting the number of processes modeled and without modifications to the existing model's parameters. Observed distributions between dissolved and particulate phases in the water column varied greatly among the metals, with average dissolved fractions being >90% for Mn,

approximately 75% for Zn, approximately 30% for Cu, and <10% for Fe. A strong seasonal trend was observed for the metals predominantly in the dissolved phase (Mn and Zn), with increasing concentrations during base-flow conditions and decreasing concentrations during spring-runoff. This trend was less obvious for Cu and Fe. Within hydrologic seasons, storm events significantly influenced in-stream metals concentrations. The most simplified modeling, using solely sorption to HFO, gave predicted percentage particulate Cu results for most samples to within a factor of two of the measured values, but modeling data were biased toward over-prediction. About one-half of the percentage particulate Zn data comparisons fell within a factor of two, with the remaining data being under-predicted. Slightly more complex modeling, which included dissolved organic carbon (DOC) as a solution phase ligand, significantly reduced the positive bias between observed and predicted percentage particulate Cu, while inclusion of hydrous manganese oxide (HMO) yielded model results more representative of the observed percentage particulate Zn. These results indicate that there is validity in the use of an existing model, without alteration and with typically collected water chemistry data, to describe complex natural systems, but that processes considered optimal for one metal might not be applicable for all metals in a given water sample.

**Water Sci Technol.** 2006;54(11-12):327-34.

Comparative toxicity of nano-scale TiO<sub>2</sub>, SiO<sub>2</sub> and ZnO water suspensions.

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TiO<sub>2</sub>, SiO<sub>2</sub> and ZnO are common additives with improved applications at the nanoscale. The antibacterial activity of TiO<sub>2</sub>, which has important ecosystem health implications, is well understood. However, less attention has been paid to the antibacterial activity of SiO<sub>2</sub> and ZnO despite them also producing reactive oxygen species. This paper explores the relative toxicity of TiO<sub>2</sub>, SiO<sub>2</sub> and ZnO water suspensions towards bacteria (*B. subtilis*, *E. coli*) and the eukaryotic *Daphnia magna*. These three photosensitive nanomaterials were hazardous to all test organisms, with toxicity increasing with particle concentration. Toxicity of the three compounds decreased from ZnO to TiO<sub>2</sub> to SiO<sub>2</sub> and *Daphnia* were most susceptible to their effects. Nominal particle size did not affect the toxicity of these compounds. Antibacterial activity was noted under both dark and light conditions indicating that mechanisms additional to ROS production were responsible for growth inhibition. These results highlight the need for caution during the use and disposal of such manufactured nanomaterials to prevent unintended environmental impacts, as well as the importance of further research on the mechanisms and factors that increase toxicity to enhance risk management.

**Chemosphere.** 2006 May;63(5):762-71. Epub 2005 Oct 5.

Extractability and bioavailability of zinc over time in three tropical soils

incubated with biosolids.

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Phytotoxicity of heavy metal is the primary concern in applying biosolids (sewage sludge) to agricultural land. This study evaluates the changes in chemical speciation of Zn in three tropical soils of Taiwan measured with sequential extraction over a one-year period. Biosolids were applied to the soils at application rates of 10, 50 and 100 Mg ha<sup>-1</sup>, and correlated diethylene triamine pentaacetic acid (DTPA) and sequential extraction as extract for prediction of Zn bioavailability to Chinese cabbage (*Brassica chinensis* L.). Experimental results indicated that the exchangeable (F1) and Fe-Mn oxide (F3) fractions in the sequential extractions increased with application rate of biosolids in the soils over time. Large amounts of Zn in the soils following the cessation of biosolids application were identified as soluble and were adsorbed by Fe-Mn oxides. The organically bound Zn, which is associated with readily decomposable carbon, is in limited amounts in the biosolid-treated soils. The DTPA-extractable concentrations of Zn in all biosolid-treated soils decreased over the time. A positive and significant correlation ( $r(2) = 0.96$ ) was found between the Zn concentrations extracted with DTPA and sum of F1 and carbonate-bound (F2) fractions in the sequential extractions. Additionally, the concentrations of Zn extracted with DTPA were strongly correlated with the concentrations of Zn in the shoots of Chinese cabbages, indicating that F1+F2 in the sequential extractions was reliable for predicting Zn bioavailability to Chinese cabbage in the biosolid-treated soils.

**Environ Monit Assess.** 2003 Jun;85(2):135-55.

Levels and speciation of heavy metals in soils of industrial Southern Nigeria.

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A knowledge of the total content of trace metals is not enough to fully assess the environmental impact of polluted soils. For this reason, the determination of metal species in solution is important to evaluate their behaviour in the environment and their mobilization capacity. Sequential extraction procedure was used to speciate five heavy metals (Cd, Pb, Cu, Ni and Zn) from four contaminated soils of Southern Nigeria into six operationally defined geochemical species: water soluble, exchangeable, carbonates, Fe-Mn oxide, organic and residual. Metal recoveries were within  $\pm 10\%$  of the independently determined total Cd, Pb, Cu, Ni and Zn concentrations. The highest amount of Cd (avg. 30%) in the nonresidual fractions was found in the exchangeable fraction, while Cu and Zn were significantly associated with the organic fraction. The carbonate fraction



contained on average 14, 18.6, 12.6, 13 and 11% and the residual fraction contained on average 47, 18, 33, 50 and 25% of Cd, Pb, Cu, Ni and Zn respectively. Assuming that mobility and bioavailability of these metals are related to the solubility of the geochemical form of the metals, and that they decrease in the order of extraction sequence, the apparent mobility and potential bioavailability for these five metals in the soil were:  $Pb > Zn > Cu > Ni > Cd$ . The mobility indexes of copper and nickel correlated positively and significantly with the total content of metals, while mobility indexes of cadmium and zinc correlated negatively and significantly with the total content of metals.

**J Environ Sci Health B.** 2001 Mar;36(2):229-43.

Accumulation and fractionation of copper, iron, manganese, and zinc in calcareous soils amended with composts.

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Amending soils with compost may lead to accumulation of metals and their fractions at various concentrations in the soil profile. The objectives of this study were to determine 1) the accumulation of Cu, Fe, Mn, and Zn with depth and 2) the distribution of water soluble, exchangeable, carbonate, Fe-Mn oxides, organic and residual forms of each metal in soils amended with MSW compost, co-compost, biosolids compost and inorganic fertilizer (as control). Total concentrations of Cu, Fe, Mn and Zn were concentrated in the 0-22 cm soil layer and scant in the rock layer. These metals were in the decreasing order of  $Fe \gg Mn > Zn > or = Cu$ . Copper, Fe, and Zn were predominantly in the residual form followed by fractions associated with Fe-Mn oxides, carbonate, organic, exchangeable and water soluble in all treatments except MSW compost amended soil where the organic fraction was higher than the carbonate fraction. In fertilizer, co-compost and biosolids compost treated soils Mn concentrated mainly in the Fe-Mn oxides form followed by residual, carbonate, and organic forms whereas, in MSW compost treated soil the same pattern occurred except that Mn organic fraction was higher than that in the carbonate form. The MSW compost has a greater potential to be used as a soil amendment to supply plants with Cu, Mn and Zn than other treatments in calcareous soils of south Florida.